Camphene as a Novel Solvent for Polypropylene: Comparison Study Based on Viscous Behavior of Solutions

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ABSTRACT: Polypropylene solutions were prepared using three solvents: paraffin oil, decalin, and a novel solvent—camphene. The effects of these solvents were evaluated based on the activation energy of flow and on their melting-point depression. Experimental results indicate that the values of the viscosity of the resulting solutions were close to Newtonian behavior in the shear rates below 34 s^{-1}. The Arrhenius–Frenkel–Eyring equation was used to describe the dependence of the viscosity on the temperature. In addition, the viscosity increased with the polymer concentration, which can be described by a power-law correlation. The activation energy of the flow of the polypropylene/camphene solution was the lowest and that of the paraffin oil solution was the highest. Correspondingly, the melting-point depression of polypropylene solutions in camphene and decalin were substantially lower than that in paraffin oil (71, 61, and 33°C, respectively). These results indicate that lower activation energies of flow correspond to higher values of melting-point depression. Moreover, analysis of variance indicated that the primary factor affecting the viscous behavior is the concentration, followed by the solvent and the temperature. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 2068–2074, 2000

Key words: camphene; polypropylene; solution; viscosity; melting-point depression

INTRODUCTION

Isotactic polypropylene (iPP) can be dissolved in hydrocarbons only at an elevated temperature.[1–3] Among these hydrocarbons, soybean oil, oleic acid, linoleic acid,[4] paraffin oil and decalin,[5] etc., are commonly used for their availability and lower cost. In a recent patent,[6] Chen used camphene as a solvent to dissolve ultrahigh molecular weight polyethylene to produce fiber with satisfactory processibility and fiber properties. In these processes, a secondary solvent, such as Freon 113 (1,2,2-trichlorotrifluoroethane), *n*-hexane, or acetone, must be used to remove these primary solvents. On the other hand, camphene is a hydrocarbon and sublimates at room temperature under atmosphere pressure. Therefore, using camphene as the primary solvent for preparing an iPP solution might make a second solvent unnecessary. This advantage not only might simplify the process, but also reduce environmental problems.
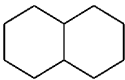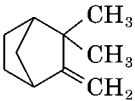
From the perspective of polymer processing, viscous behavior affects the processibility of the polymer solution. The entanglement concept[7,8] indicates that the viscosity depends on the formation of entanglement. In addition, the strength of entanglement depends on the interaction between polymer chains and the solvent molecules or on the value of the friction factors. A good solvent can facilitate the extension of the polymer

Table I Properties of Solvents Used in This Work

Solvent	Molecular Structure	Molecular Formula	Mp (°C)	Bp (°C)	η at 130°C (mPa s)
Paraffin oil	Alkanes	C_nH_{2n+2} $n=16–30$[a]	−10–3 (mixture)	273–367 (mixture)	2.30
Decalin		$C_{10}H_{18}$	−43.2	195.7	0.60
Camphene	CH_3 CH_3 CH_2	$C_{10}H_{16}$	51.5	159	0.54

[a] Based on the analysis of GC-mass.

chain and reduce the possibility of entanglement formation of the polymer chain. Thermodynamically, a good solvent can cause a higher melting-point depression.[9]

In light of the above considerations, this study used camphene as a solvent for preparing an iPP solution. In addition, the solvent effect under various concentrations and temperatures was compared with those solutions of decalin and paraffin oil in terms of viscous behavior and melting-point depression since both concentration and temperature are the major operating parameters. The results are summarized into empirical correlation and were analyzed by the ANOVA method. Results presented herein can hopefully be used to analyze their flow properties in polymer processes such as membrane manufacturing and film casting to obtain appropriate processing conditions.

EXPERIMENTAL

Materials

Polypropylene (Profax 6331, M_w = 206,887) was obtained from the Taiwan Polypropylene Co. (Taipei, Taiwan). Decalin and the antioxidant 2,6-di-t-butyl-4-methyl cresol (BHT) was purchased from Ferak (Berlin, Germany). Camphene was obtained from Merck (Hohenbrunn, Germany), and paraffin oil was obtained from Fisher Chemical (Fair Lawn, NJ). Properties of the solvents used in this work are listed in Table I. All these chemicals were used as received without further purification.

Preparation of Polypropylene Solution

Polypropylene chips were added into a solvent according to the specified concentration. The liq-uid mixture was slowly stirred at 135–175°C for 90 min (depending on the solvent). To prevent polymer degradation, 1 wt % of BHT based on polypropylene was also added to the solution. The flask was purged with nitrogen as well.

Viscosity Measurement

The viscosity of the polypropylene solutions was measured using a Brookfield viscometer (Model LVDV1+) with three spindles to cover the different ranges of viscosity. These measurements were taken within the temperature range of 110–160°C, which was controlled by a thermal barrel.

DSC Measurement

The melting-point depression of the iPP solutions was measured using differential scanning calorimetry (DSC; TA 2000, DuPont, USA). The specimens were all of a 20% iPP solution. The weight of the specimens for DSC was about 10 mg. To prevent loss of the solvent, a volatile sample pan was used. The measurement started at 30°C, and the heating rate was 10°C/min, held at 155–185°C for 30 min (depending on the solvent) and then cooled at the same rate. The melting peak during the second heating cycle was taken as the melting point of the mixture.

RESULTS AND DISCUSSION

Flow Curve

Figure 1 depicts the flow curves of iPP in decalin, paraffin oil, and camphene at130°C. Due to the limitation of the viscometer, the strain rate ranges between 0.1 and 34 s^{-1}. According to this
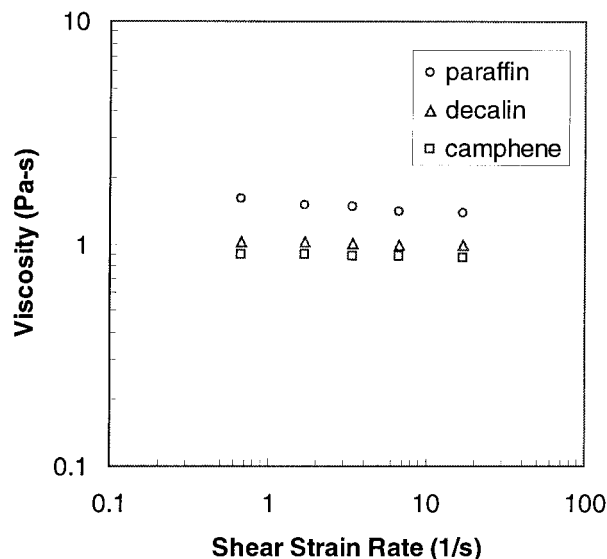
Figure 1 Flow curves of iPP solutions in different solvents at strain rate below 40 s^{-1}. Temperature: 130°C; concentration: 15 wt %. (○) Paraffin oil; (△) decalin; (□) camphene.

figure, these data are falling on straight lines. These data were correlated with the power-law model as follows:

$$\eta = m \ \dot{\gamma}^{n-1} \qquad (1)$$

where m denotes the consistency and n is known as the flow index.[8,10] Herein, we correlated these data with eq. (1) by linear regression to obtain m and n. Table II summarizes those results. Figure 1 plots the fitted lines. According to this figure, the values of n are extremely close to 1. This finding suggests that the viscous behavior of these polymer solutions is in the Newtonian plateau. Therefore, the consistency m can be regarded as the zero-shear viscosity, η_0, in the following discussion.

Effect of Temperature on Viscosity

According to previous literature, viscosity depends on the temperature according to the Arrhenius–Frenkel–Eyring (AFE) equation[8]:

$$\eta = k \ \exp(\Delta E/RT) \qquad (2)$$

where ΔE denotes the activation energy of flow and R is the gas constant. Figure 2 confirms this dependence, where the zero-shear viscosity, η_0, was plotted versus the reciprocal of the tempera-

ture. As Table II indicates, the values of the power-law index n are extremely close to 1. Figure 2 reveals that the zero-shear viscosity of the iPP–paraffin oil solution is higher than that of the other two solutions. This observation suggests that the Newtonian behavior of this iPP solution

Table II   Fitted Power-law Parameters

Solvent	C (wt %)	T (°C)	m	n
Paraffin oil	5	130	0.038	1.02
		140	0.028	1.07
		150	0.026	1.03
	10	130	0.358	0.963
		140	0.284	0.968
		150	0.238	0.970
	15	130	1.560	0.954
		140	1.262	0.946
		150	1.011	0.952
	20	130	5.594	0.935
		140	4.527	0.934
		150	3.876	0.948
	25	130	15.444	0.931
		140	11.404	0.963
		150	8.909	0.971
Decalin	5	130	0.023	1.00
		140	0.021	1.00
		150	0.018	1.00
	10	130	0.283	1.00
		140	0.243	0.982
		150	0.217	0.988
	15	130	1.020	0.988
		140	0.884	0.986
		150	0.782	0.980
	20	130	2.584	0.975
		140	2.117	0.963
		150	1.789	0.979
	25	130	8.625	0.952
		140	7.000	0.966
		150	5.685	0.960
Camphene	5	130	0.018	1.00
		140	0.016	1.00
		150	0.014	1.00
	10	130	0.194	0.994
		140	0.168	0.986
		150	0.158	0.993
	15	130	0.905	0.990
		140	0.778	0.992
		150	0.675	0.999
	20	130	2.959	0.957
		140	2.414	0.960
		150	2.130	0.968
	25	130	8.043	0.970
		140	6.257	0.968
		150	5.906	0.966
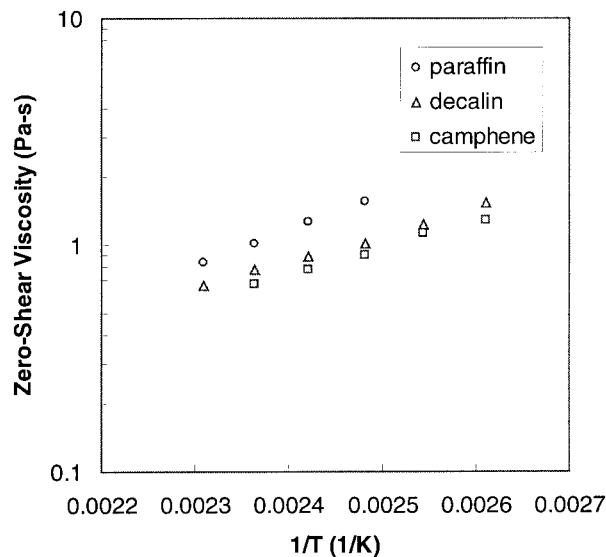
Figure 2 Dependence of η_0 of iPP solutions on temperature. Concentration: 15 wt %. (○) Paraffin oil; (△) decalin; (□) camphene.

Figure 3 Dependence of η_0 of iPP solutions on concentration. Temperature: 130°C. (○) Paraffin oil; (△) decalin; (□) camphene.
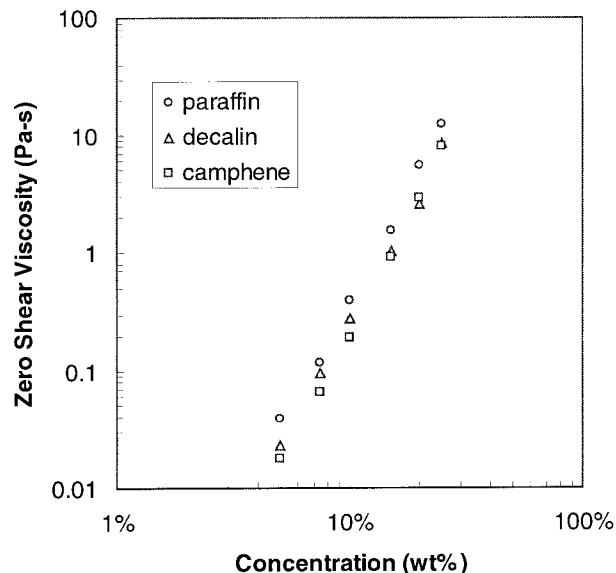
only slightly changes in the temperature range between 110 and 160°C. This figure also reveals that all the curves are approximately straight lines. Each line corresponds to a solvent. The two straight lines of decalin and camphene are approximately parallel to each other, implying that these two solvents resemble each other in terms of the effect of temperature.

Effect of Concentration on Viscosity

Several attempts have been made to derive predictive relationships for the Newtonian viscosity of concentrated solutions of flexible polymers. In the textbook of ref. 8, the viscosity of a polymer solution is known empirically to depend on the concentration in a power-law fashion:

$$\eta = K \, c^\alpha \tag{3}$$

where c denotes the concentration and α is a constant. According to Figure 3, the η_0 of each solvent falls on a line versus the concentration. This observation confirms that the viscosity of the iPP solution follows eq. (3). Actually, the factor K should also include the effect of the molecular weight. However, in this study, we did not use the sample of other molecular weights and, hence, the molecular weight effect was hidden in the factor K.

Combined Effect of Concentration and Temperature on Zero-shear Viscosity

By taking the linear regression on the values of η_0 against both the temperature and the concentration, we obtained the following correlation:

$$m = k \, c^\alpha \exp(\Delta E/RT) \tag{4}$$

where ΔE and α were determined by the least-square method. Table III tabulates the fitted values of k, α, and ΔE. For data plotting, we rearranged eq. (4) as follows:
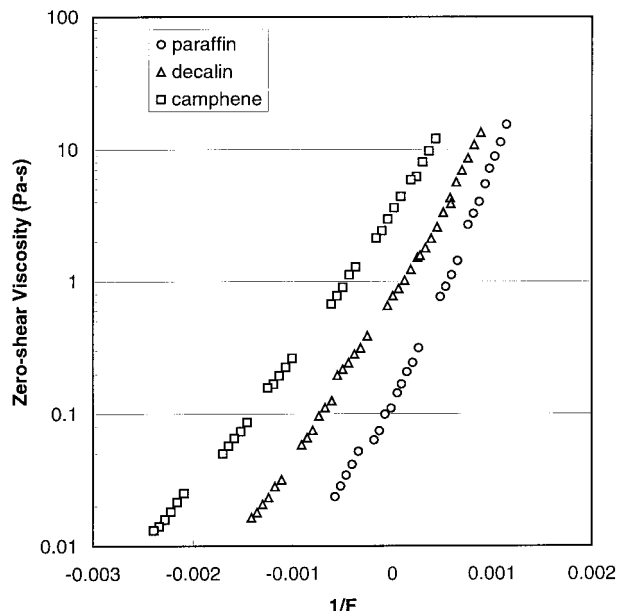
$$m = k \exp(\Delta E/RF) \tag{5}$$

where F is defined as

$$\frac{1}{F} \equiv \frac{1}{T} + \frac{R\alpha}{\Delta E} \ln(c) \tag{6}$$

Table III   Fitted k, α, and ΔE in Eq. (4)

| Solvent	k	α	ΔE (kJ/mol)	R^2
Paraffin oil	0.426	3.74	28.71	0.992
Decalin	0.811	3.57	23.87	0.997
Camphene	3.34	3.78	20.01	0.997

Figure 4 Master curves of η_0 of iPP solutions in different solvents. (○) Paraffin oil; (△) decalin; (□) camphene.

The viscosity data are plotted in Figure 4 and show that they can form three master curves. According to this figure, these three master curves are nearly linear, but with different slopes for each solvent. The values of ΔE in Table III indicate that the iPP solution in camphene has the lowest activation energy and that in paraffin oil is the highest.

As generally known, the activation energy of flow in a poor solvent is higher than that in a good solvent[8] because the entanglement is stronger due to stronger polymer–polymer interaction in a poor solvent. Therefore, the use of paraffin oil makes the iPP solution poorer than that of camphene. In a poorer solvent, the polymer–polymer interaction is stronger than is the polymer–solvent interaction. When the iPP is dissolved in paraffin oil, the occurrence of the disentanglement effect is less than that in camphene.

We believe that the difference in the viscous behavior in these three solvents is due to the molecular structures.[11] As shown in Figure 5, paraffin oil is a mixture of alkanes, decalin is a bicyclic molecule, and camphene has a stereotricyclic structure. For polymeric liquids, the viscosity increases with the entanglement density.[8] The probability of forming an entanglement decreases with an increasing intermolecular distance between the polymer chains.[7,8] In Figure 5, the diameter of the shortest axis of camphene (if we
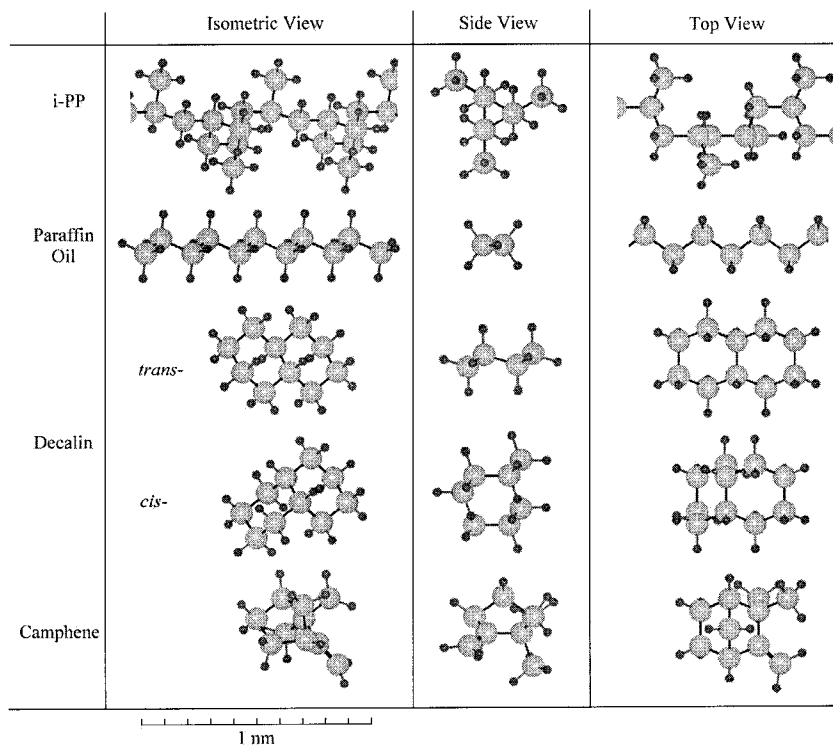
Figure 5 Molecular models of iPP, paraffin oil, decalin, and camphene.

Table IV Melting-point Depression of 20% iPP Solutions

Solution	T_m (°C)	ΔT_m (°C)
iPP–paraffin oil	141	33
iPP–decalin	113	61
iPP–camphene	103	71
iPP	174[a]	—

[a] Equilibrium melting point of iPP, from ref. [12].

approximate it as a ellipsoid) is the largest; hence, it can provide the largest distance between the iPP molecules, and, thus, entanglement is most difficult to form. The size of *cis*-decalin is close to that of camphene, while that of *trans*-decalin is smaller. On average, the intermolecular distance of iPP in decalin would be slightly less than that in camphene. On the other hand, the size of paraffin oil is the smallest. It can easily be fitted into the intramolecular gaps of the iPP helical structure. Hence, in paraffin oil, the intermolecular distance of iPP chains is substantially smaller than that in the other two solvents. This makes the possibility of entanglement formation higher in paraffin oil. Therefore, the viscosity of the iPP solution in paraffin oil is higher than that in decalin and camphene.

Melting-point Depression

The conformation of the polymer chain may be changed during solution formation, which may cause the enthalpy to vary with the interaction between the polymer and the solvent. This change in enthalpy is usually expressed as the χ value (Flory interaction parameter). However, paraffin oil, a conventionally used solvent for polyolefins, is a mixture containing C_{16}–C_{30} alkane isomers. This feature makes it difficult to calculate the χ value between paraffin oil and iPP. Instead, based

on practical applications, the melting-point depression of the iPP solution is chosen as the criteria for comparison in this study.

Table IV indicates that the melting point of iPP mixes with different solvents. The iPP–paraffin solution has a much higher melting point (141°C) than those of the iPP–decalin (113°C) and iPP–camphene (108°C) solutions. By subtracting from the equilibrium melting point of pure iPP (174°C),[12] their corresponding melting-point depressions are 33, 61, and 71°C, respectively. This finding suggests that camphene and decalin have a higher compatibility to the iPP molecules than that of paraffin oil. The molecular structure difference mentioned above accounts for why this occurs, thereby correlating with the results of the viscosity measurement.

Analysis of Variance of Experimental Results

To identify the priority of the solvent, concentration, and temperature, analysis of variance (ANOVA) was performed.[13] ANOVA is a statistical method frequently used in engineering to justify the priority of influencing factors based on the F-test. Table V summarizes those results. This table reveals that the concentration is the most significant factor affecting the viscosity in the concentration ranging from 5 to 25%. The solvent is the next significant factor among paraffin oil, decalin, and camphene, followed by the interaction of the concentration and the solvent with temperature in the range of 130–150°C and the interaction of the temperature and concentration. Notably, the interaction of the solvent and temperature is insignificant.

CONCLUSIONS

This study demonstrates that the strain-rate dependency of the viscosity of iPP solutions in cam-

Table V ANOVA

Source	Sum Square	df	Mean Square	F	$F(0.05)$	Conclusion
A (solvent)	25.77	2	12.88	43.62	3.63	Significant
B (temperature)	9.675	2	4.83	16.38	3.63	Significant
C (concentration)	458.23	4	114.55	387.84	3.01	Significant
$A \times B$	1.23	4	0.31	1.04	3.01	Insignificant
$A \times C$	35.92	8	4.49	15.20	2.59	Significant
$B \times C$	15.47	8	1.93	6.55	2.59	Significant
E	4.72	16	0.30			

phene, decalin, and paraffin oil can be correlated with the power-law model. However, the power-law index n is close to 1 when the strain rate is below 34 s^{-1}. This finding suggests that these solutions are Newtonian at this range of the strain rate.

At this Newtonian plateau, the zero-shear viscosity, η_0, depends on the temperature following the Arrhenius formula. In addition, the viscosity increases with the concentration. The combined effects of temperature and concentration on the zero-shear viscosity show a nearly linear correlation for iPP solutions in the solvents used. Among them, the iPP–paraffin solution has the highest activation energy of flow and camphene has the lowest activation energy. An explanation based on molecular models was proposed for the effect of the solvent on the viscous behavior. To verify this concept, the melting-point depression was employed. Experimental results indicate a similar trend in the compatibility of these three solvents to iPP.

On applying ANOVA to the experimental results, the concentration is the most significant factor affecting the viscosity. The solvent is the next significant factor, followed by the interaction of the concentration and solvent with temperature and the interaction of the temperature and concentration. Furthermore, the interaction of the solvent and temperature is insignificant.

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